

Evidence of local magnetic order in hcp iron from Raman mode splitting

Gerd Steinle-Neumann,^{1,*} Lars Stixrude,¹ R. E. Cohen,² and Boris Kiefer¹

¹*Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109-1063*

²*Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015-1035*

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Experimental measurements of Raman spectra for hcp iron at high pressure show two modes over a considerable pressure range in contrast to the prediction of one doubly degenerate mode for the hcp lattice. We use density functional theory to investigate the influence of magnetic order on the Raman active modes of hcp iron. We find an antiferromagnetic state that lifts the degeneracy of the transverse optical mode, and yields stable antiferromagnetic moments up to approximately 60 GPa (55 Bohr³). The resulting frequencies of the two transverse optical modes are in good agreement with the experimental Raman shifts, lending support to the existence of local antiferromagnetic order in hcp iron.

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The presence of magnetism strongly influences material properties and phase relations in the 3d transition metals. This is particularly true for iron where the competition between magnetic and non-magnetic contributions to the internal energy, differences in the vibrational and magnetic entropy, and differences in volumes all contribute to phase stability [1]. Ferromagnetism stabilizes the body centered cubic structure over the close packed phases at ambient condition [2], and an understanding of the spin-density wave ground state in its high temperature polymorph, cubic close packed (fcc), has important implications on its physical properties [3]. Magnetism in the high pressure polymorph, hexagonally close packed (hcp), is less well characterized and has long been thought to be absent, but its proposed presence [4] may play an important role in our understanding of material properties at pressure, with applications to the study of planetary interiors [5] and impact phenomena.

The hcp lattice has two atoms per unit cell giving rise to optical phonon modes through Brillouin zone folding. Advances in experimental techniques have made it possible to measure the Raman active transverse optical (TO) mode in iron through optical spectroscopy [6, 7]. In contrast to the fundamental prediction that this mode (E_{2g}) be doubly degenerate, one set of experiments at high pressure show two peaks in the Raman spectrum up to pressures of 40 GPa [6]. While amplitude and sharpness of the two peaks differ significantly, this observation nonetheless suggests that the symmetry of hcp iron is lower than the atomic arrangement; spin-phonon interactions provide a symmetry-breaking mechanism. Based on first principles theory the lowest energy state found to date is an anti-ferromagnetic (afm) structure with orthorhombic symmetry and four atoms in the unit cell (afmII) [4]. The afmII structure corresponds to a spin wave with wave vector $q = (0, 1/2, 0)$, at the M point on the Brillouin zone boundary (Fig. 1). This structure has been predicted to be stable for hcp iron up to pressures of almost 60 GPa [4]. The magnetic structure results in two

TO zone center modes (A_{2g}) both of which are Raman active.

Here we investigate the influence of afmII ordering on the zone center TO phonon mode over the compression range where finite moments are predicted (≥ 60 Bohr³/atom). We calculate the zone center Raman frequencies by the frozen phonon approximation: energy changes are evaluated in response to small displacements along the phonon eigenvector, the second order term yielding the frequency. We base our analysis on to-

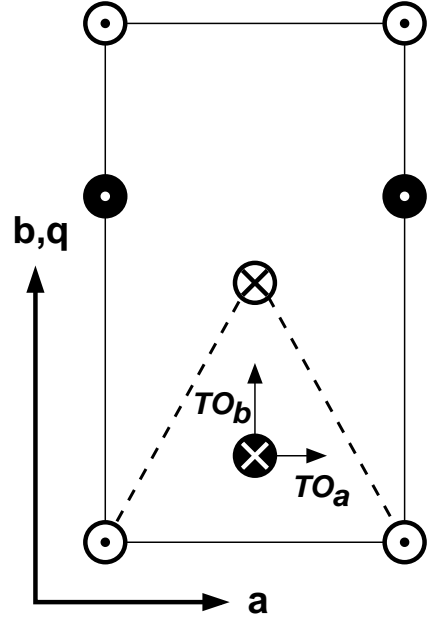


FIG. 1: Orthorhombic antiferromagnetic groundstate of hcp iron (afmII). Open circles show the atomic positions at $z=1/4$, filled circles at $z=3/4$ with the arrows indicating the direction of spin on the atoms. The orthorhombic unit cell is outlined with the axes given. The direction of the wavevector q for the afmII spinwave is along the b -axis. The a - and b -axes also define the eigenvectors for the TO modes (TO_a and TO_b). The c -axis is out of the plane.

tal energies obtained with the full-potential linearized-augmented plane-wave method (LAPW) [8] using a generalized gradient approximation [9] to the exchange correlation potential. We treat $3s$, $3p$, $3d$, $4s$, and $4p$ states as valence electrons for all volumes and use $R_{MT}=2.0$ Bohr for the muffin tin radii, $R_{MT}K_{max} = 9.0$, a $12 \times 6 \times 12$ special k-point mesh, and a temperature broadening of 5 mRy. With this set of computational parameters we have previously established convergence of relative energies to within 0.1 mRy/atom and magnetic moments to better than $0.05 \mu_B/\text{atom}$ [4]. The TO modes are characterized by displacements of the close packed planes with respect to one another. The eigenvectors for the the two A_{2g} modes in the afmII structure are along the orthorhombic a - and b -axes (Fig. 1). For comparison we also compute the TO mode frequency for the non-magnetic case. To efficiently evaluate the energetics of the system we fixed the axial ratio in our calculations to $c/a = 1.6$, close to the experimentally [10, 11] and theoretically [4] estimated equilibrium value.

Inspection of the afmII structure reveals that fundamentally different spin interactions are involved in the two TO modes (Fig. 1). For displacements along the orthorhombic a -axis (TO_a) atoms approach nearest neighbors with unlike spin. For displacements along the orthorhombic b -axis (TO_b) atoms alternately move towards a nearest neighbor with like spin and towards a pair of nearest neighbors of opposite spin. The resulting energy-displacement relations reflect the antiferromagnetic spin interactions (Fig. 2): for unlike spins approaching the energy is reduced with respect to the non-magnetic case, and for same spin nearest neighbor interactions (along positive b) there is an additional repulsion. The calculated equilibrium magnetic moments are consistent with these findings (Fig. 2): They increase for displacements along a , as they do along negative b ; for positive b they decrease considerably as the like spin nearest neighbors approach.

We find that the TO_a mode frequency agrees well with that of the lower frequency, higher amplitude peak found in the Raman experiments, and that the TO_b mode frequency corresponds to the experimentally observed satellite peak at higher frequency (Fig. 3). The magnitude of the predicted TO mode splitting decreases as the afm moment is reduced by compression, in excellent agreement with the observation in the Raman experiments (Fig. 3). The magnitude of splitting is related to the directionality of the spin wave considered here (with wave vector M), but other spin waves with wavevectors along high symmetry directions in the base of the hexagonal Brillouin zone will generally result in splitting of the TO mode. The systematic offset of the calculated frequencies by approximately 20 cm^{-1} ($< 10\%$) is typical for a comparison of computed and measured phonon frequencies [12, 13].

Spin-phonon interactions have been found to have

a strong effect on Raman scattering in a number of systems, including cupric oxide [14] and the copper-ruthenium oxide $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ [15]. The general character of the effect of spin-phonon interaction on the Raman spectra in these materials is consistent with the observations for hcp iron: broad, low amplitude, satellite peaks appear as the sample is cooled below the Curie or Neel temperature, upon further cooling such peaks generally sharpen and gain amplitude as the degree of magnetic ordering increases. Observation of an increase in amplitude of the satellite peak in hcp iron upon cooling would lend support to the predicted magnetic structure.

Other experimental investigations of possible magnetic states in hcp iron have been inconclusive. Magnetism in hcp iron exists at over-expanded volumes in epitaxially grown multilayers on a ruthenium substrate [16] although the nature of the spin ordering is still controversial [17, 18]. Nuclear X-ray absorption experiments [19] show significant loss of moment across the phase transition from fcc to hcp iron, but do not unambiguously

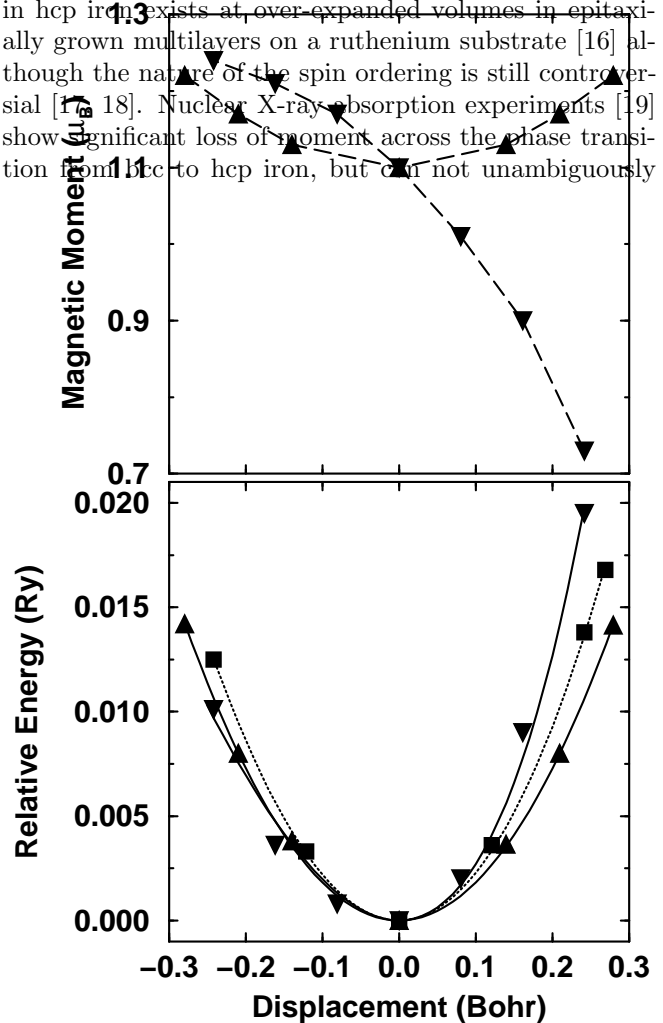


FIG. 2: Energy of displacement of hcp iron at $V=70 \text{ Bohr}^3/\text{atom}$ in the lower panel. Relative energy changes as a function of displacement for the non-magnetic structure (squares), and the afmII structure for displacements along TO_a (triangles up) and TO_b (triangles down). Dotted and solid lines are third order polynomial fits to the results. The upper panel shows the change in the afmII moment as a function of displacement for TO_a and TO_b (same symbols, dashed-line to guide the eye).

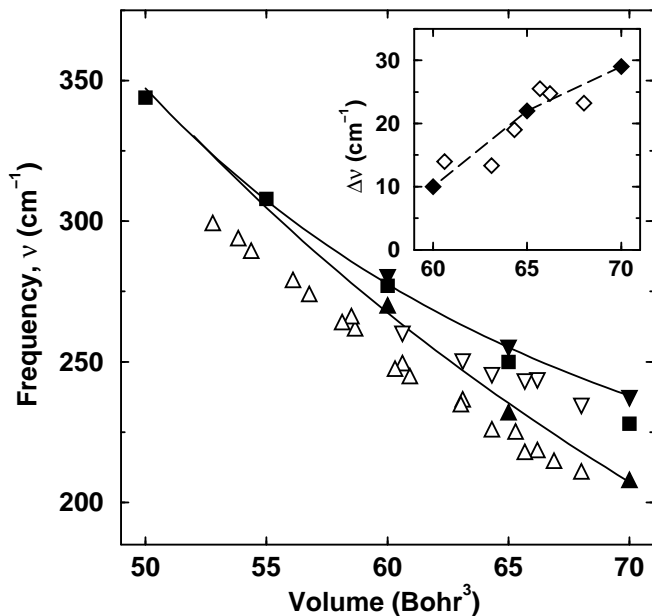


FIG. 3: Raman frequencies as a function of atomic volume. Non-magnetic calculations are shown in filled squares. The afmII structure results in transverse optical frequencies (filled triangles) with TO_a being the lower (up) and TO_b (down) the upper branch. The solid lines through TO_a and TO_b are third order polynomial fits in $V^{-2/3}$. Experiments (Ref. 6) identify two peaks in the Raman spectra up to 40 GPa in open symbols. The stronger peak is shown in the triangles up, and the weaker peak in triangles down. The inset compares the split in Raman frequencies from theory (filled diamonds) and experiment (open diamond).

be interpreted to show no moments in the high pressure polymorph: the change in absorption spectra is due to changes in the density of states as well as to spin related satellites. Diamond anvil cell in-situ Mössbauer measurements on hcp iron have not shown any ordered magnetic ground state in its stability field [20, 21, 22, 23] but it was recognized that magnetism cannot unambiguously be ruled out based on the data [20, 22]. The Mössbauer data suggest that correlation times of spin fluctuations must be relatively short, or that competing contributions to the effective field cancel each other as is the case in CaRuO_3 perovskite [24, 25]. The in-situ observation of super-paramagnetism in hcp-Fe [22] may support the notion that the effective field is approximately cancelled, and suggests, following the procedure of Felner *et al.* [25], a Mossbauer experiment on an appropriately doped hcp-Fe sample (e.g. with Ru). The inherent frustration of the triangular lattice might lead one to suspect more complex spin arrangements than those considered here, such as incommensurate spin waves, as in the case of fcc iron [3, 26], non-collinear structures, spin glass, or a combination of these [27].

Acoustic modes can also be influenced by spin-phonon interactions as is evidenced by anomalous phonon disper-

TABLE I: Raman shift for hcp iron for the non-magnetic E_{2g} mode and the two antiferromagnetic TO modes (A_{2g} : TO_a , TO_b) as a function of atomic volume. Pressure P is from the afmII equation of state (Ref. 4).

Volume (Bohr ³)	P (GPa)	ν (E_{2g}) (cm ⁻¹)	ν (TO_a) (cm ⁻¹)	ν (TO_b) (cm ⁻¹)
70	2	228	208	237
65	22	250	232	254
60	55	277	270	280
55	109	308	—	—
50	193	344	—	—

sion in fcc iron near the zone center [28]. Indeed we find that the afmII ordering also influences the compressional properties of hcp iron [4]: the bulk modulus at pressure is reduced, bringing it in closer agreement with experimental data [10, 11] than non spin-polarized calculations. Better agreement of aggregate elastic properties between afmII and experimental data lends further, independent, support to the presence of magnetism in hcp iron.

The possible existence of magnetic correlations in hcp iron may be important in our understanding of the recent observation of superconductivity in hcp iron under pressure [29]. Long thought to be antithetical, superconductivity and magnetism have recently been observed simultaneously in a number of systems [30, 31, 32]. Of particular interest is the observation for ZrZn_2 where magnetism and superconductivity appear to be directly coupled [31] as is evidenced by the loss of superconductivity and magnetism at the same pressure, leading to the speculation that hcp iron might behave similarly [33].

In conclusion, we report first-principles results on the zone center TO phonon frequency of hcp iron for non-magnetic and afm structures at ambient and high pressure from a frozen phonon calculation. We find good agreement with experimental results for the absolute frequencies, and spin-phonon interactions provide a quantitative explanation for the split of the TO mode in hcp iron which is observed up to a pressure of 40 GPa. In combination with a considerably better agreement of elastic properties between experiment and the orthorhombic afm structure, as compared to non-magnetic calculations, this suggests that magnetism may play an important role in the physical behavior of hcp iron at high pressure.

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- * g.steinle-neumann@gl.ciw.edu; now at: Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015-1035
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